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TANNING WITH GLUTARALDEHYDE

II. PROPERTIES OF THE LEATHERS*

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ABSTRACT

Sheepskins were tanned with glutaraldehyde under various conditions. The tanned skins were processed with regular packs into finished garment leather in a commercial tannery. Leather judged to be quite satisfactory was obtained under a wide variety of tanning conditions. The leathers showed unusual resistance to deterioration by a synthetic perspiration and by hot soap solutions, in contrast to formaldehyde and glyoxal leathers.

INTRODUCTION

The preceding paper (1) reported a study of the tanning properties of glutaraldehyde, a newly available dialdehyde. This aldehyde appeared to be unusually reactive toward hide substance and exhibited tanning properties of value from a practical standpoint. It effects tanning over a wide pH range. The tannage is rapid and may be accomplished within a few hours with as little as 1.5% of active aldehyde on the drained pickled skin basis. To evaluate this tannage fully it was important to examine the properties of the leathers produced with glutaraldehyde. Of particular interest was a comparison of this leather with that obtained with formaldehyde. In the present study, full sheepskins were tanned with the desired aldehyde in the laboratory and then processed into finished leather in a commercial tannery with regular packs of garment leather. The results are reported in this paper.

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EXPERIMENTAL

Twenty-Four-Hour Tannages

Pickled, degreased Syrian sheepskins obtained from a garment leather tannery were tanned with glutaraldehyde for 24 hours under various conditions as described in the preceding study (1). The identical skins obtained at the end of the 24 hours of tanning in the rate studies were used. The tanned skins were washed briefly in running water; acidified, if necessary, with dilute acetic acid to pH of about 5; and processed into finished leather with regular packs at a garment leather tannery.

For purposes of comparison, Syrian sheepskins were also tanned with formaldehyde at pH values of approximately 4.8, 8.0, and 9.4 and with glyoxal at pH 8.1 as described previously (1). These tannages were carried out exactly as was done for the glutaraldehyde except for replacing the 12% glutaraldehyde (25% solution) with an equivalent amount of formaldehyde or glyoxal. The leathers were finished in the same manner as those above.

The various tannages are summarized in Table I.

Evaluation of the leather.—Chemical analyses, strength properties, perspiration resistance, and washability tests were carried out on the finished leathers. The test pieces were taken from the same skin location, which was essentially equivalent to Test Area "W" described in *Sampling Light Leather for Physical Tests* (2).

Perspiration resistance—Samples cut from the finished leathers were tested for perspiration resistance by a slight modification of the procedure described by Colin-Russ (3). Briefly, small pieces of leather were soaked about 2 hours in a synthetic perspiration solution made up of urea, sodium lactate, disodium phosphate, sodium chloride, and water. Acid or alkali was added if necessary to bring the pH to 7.0–7.1. The saturated pieces of leather were held over water in a closed vessel at 70°C. for 48 hours. After air-drying, the dimensions of the samples were measured and percentage area shrinkage calculated. Results are summarized in Table II.

Washability—The washing test, to determine the stability of the tannage to the effects of hot, soapy water, was run in a "Launder-Ometer"* similarly to the test applied to textiles (4). This machine holds pint jars containing the soap solution and leather samples together with steel balls for mechanical action, and tumbles them end over end in a thermostatically controlled water bath. The data shown in Table II give results obtained by washing 3 pieces of leather (2″ x 2½″ each) in 200 ml. of 0.5% Ivory soap solution (pH about 10). The washing cycle was for ½ hour at 120°F. All three samples were

*Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

TABLE I

LEATHERS FROM 24-HOUR TANNING OF SYRIAN SHEEPSKIN

No.	Tannage[a] Aldehyde[b] %DPW	pH[c]	Aldehyde Consumed[d] %	Ts of Leather Tanned °C.	Ts of Leather Finished °C.	Analysis (MFB)[e] N %	Fat %	Ash %	Hide Subs. N × 5.62 %	Balance %	Fixed Aldehyde[f] mmoles/gHS
					Glutaraldehyde, 25% solution						
1	6	2.4	55	72	71	12.06	26.10	0.52	67.78	5.60	0.33
2	10	2.5	50	77	73	12.80	23.17	0.46	71.94	4.43	0.50
3	12	4.1	74	81	77	12.73	19.93	0.79	71.54	7.74	0.89
4	24	4.1	38	80	77	11.51	25.28	0.89	64.67	9.16	0.91
5	6	5.1	90	81	76	12.17	25.80	0.49	68.40	5.31	0.54
6	12	5.0	70	82	76	11.63	26.43	0.72	65.36	7.49	0.84
7[g]	12	4.8	63	81		11.44	26.96	1.12	64.29	7.63	0.76
8	24	5.0	46	82	78	11.50	26.30	0.51	64.63	8.56	1.10
9	6	6.3	95	77	74						
10	6	6.3	96	79	77	12.37	23.70	0.48	69.52	6.30	0.58
11	12	6.4	90	82	77	12.28	22.90	0.44	69.01	7.65	1.08
12	24	6.1	56	82	78	11.56	25.43	0.47	64.97	9.13	1.34
13	6	8.3	98	81	76	11.92	24.25	0.49	66.99	8.27	0.59
14	6	8.4	99	82	77	12.88	21.05	0.42	72.39	6.14	0.59
15	12	8.4	95	82	79	13.16	19.07	0.42	73.96	6.55	1.14
16	24	8.2	66	78	78	11.55	25.33	0.47	64.91	9.29	1.58
17	6	9.8	99	77	78	11.88	26.00	0.52	66.71	6.71	0.58
18	12	9.2	97	83	77	11.86	24.60	0.50	66.65	8.25	1.16
19	24	9.0	91	81	79	12.44	19.73	0.49	69.91	9.87	2.18
					Formaldehyde, 37% solution						
20	4.9	4.8	34	78	72	11.22	30.43	0.90	63.06	5.61	0.82
22	4.9	8.0	44	83	79	12.34	24.80	0.86	69.35	4.99	1.06
23	4.9	9.4	49	84	78	12.83	21.83	0.94	72.10	5.13	1.18
					Glyoxal, (pure) 30% solution						
24	5.8	4.8	6	58	No tanning effect						0.07
25	5.8	8.1	72	75	73	11.36	28.38	1.19	63.84	6.59	0.86

[a] For details of tanning refer to same experiment number in Table I of preceding paper (1).
[b] As the aqueous solution of commerce. DPW signifies drained pickle weight.
[c] Value at end of 24-hours tanning.
[d] Calculated from the initial and final concentration of aldehyde in tanning liquor. Expressed as percent of aldehyde input.
[e] Analysis of finished leather.
[f] Fixed aldehyde at equilibirium was calculated from aldehyde consumed; assuming 25% of drained pickled weight to be hide substance.
[g] 200% water instead of 100% as in others.

TABLE II

PROPERTIES OF SYRIAN SHEEPSKIN TANNED WITH GLUTARALDEHYDE

Exp. No.	Tannage[a] %DPW	Tannage[a] pH	Ts[b] °C.	Washability Ts, °C. after Wash 1	2	3	ΔTs[c] °C.	Perspiration Resist. Shrinkage, %	Stitch-Tear Strength Parallel lb.	Parallel lb/in	Perpendicular lb.	Perpendicular lb/in
						Glutaraldehyde						
1	6	2.4	71	65	65	63	8	77	22.5	589	22.3	535
2	12	2.5	73	66	67	66	7	65	23.9	450	30.3	527
3	12	4.1	77	73	71	71	6	34	13.6	227	13.6	259
4	24	4.1	77	76	74	73	4	21	9.5	223	4.4	131
5	6	5.1	76	74	72	67	9	24	26.5	629	28.5	571
6	12	5.0	76	76	74	70	6	4	20.1	464	17.2	376
8	24	5.0	78	77	76	73	5	3	16.4	416	21.4	499
9	6	6.3	74					34	23.2	427	28.5	533
10	6	6.3	77	78	73	73	4	4	11.7	310	15.3	401
11	12	6.4	77	76	75	73	4	1	19.2	456	21.2	499
12	24	6.1	78	77	77	75	3	1	22.1	376	20.1	376
13	6	8.3	76	74	74	71	5	34	20.1	444	20.1	426
14	6	8.4	77	77	73	72	5	6	16.6	454	17.9	494
15	12	8.4	79	80	78	77	2	3	30.3	442	30.5	414
16	24	8.2	78	78	76	75	3	1	13.3	291	16.1	305
17	6	9.8	78	76	75	71	7	48	16.1	333	13.9	312
18	12	9.2	77	78	77	73	4	1	29.2	442	32.7	464
19	24	9.0	79	78	77	74	5	1	20.1	426	20.8	462
						Formaldehyde						
20	4.9	4.8	72	67	65	61[d]	11	[e]	14.8	376	18.5	417
22	4.9	8.0	79	74	73	66	13	[e]	27.1	485	27.3	451
23	4.9	9.4	78	74	73	71	7	[e]	30.4	548	19.2	397
						Glyoxal						
25	5.8	8.1	73	67	67	67[d]	6	77	7.9	288	14.3	466

[a] For details refer to same experiment number in Table I. pH is value at end of 24 hours.
[b] Ts of finished leather.
[c] ΔTs refers to the change in the Ts after three washes.
[d] The washed leather samples from these tests were very stiff, and mechanical action showed but little improvement in softness.
[e] Completely unstable.

washed together and given three wash cycles, the specimens being rinsed and air-dried after each cycle. The shrink temperature (Ts) of the washed samples was determined after each cycle. The air-dried leathers after each wash were also examined for leather character.

Strength properties—Specimens were cut from the selected test area (W) for determination of stitch-tear strength. The same location on each skin was chosen, and two adjacent specimens were tested. The double-hole stitch-tear test method (5) was used, and the data are shown in Table II.

Analyses—The leathers were ground in a Wiley mill, and standard methods of analysis were employed. Total nitrogen was determined by the semi-micro Kjeldahl method (6). Moisture and ash were determined by the official ALCA methods (7). The fat content of the finished leathers was determined after hydrolysis of the leather sample (8). The leather was hydrolyzed by refluxing in 4*N* HCl, and the hydrolyzate was extracted with Skellysolve B. Evaporation of the solvent gave an estimate of oil content. This procedure gave fat values 2 to 4% higher than those obtained by chloroform extraction of the leather (9).

The results are summarized in Table I.

Eight-Hour Tannages

The 24-hour tannage was used to study the rate of reaction of glutaraldehyde with collagen. From a practical standpoint a shorter time is desirable. Precautions must be taken, however, to avoid drawing the grain from too rapid a tanning action at the beginning. This can be accomplished by adding the glutaraldehyde in feeds or by controlling the pH. The procedures outlined below produced smooth-grained, well-let-out sheepskin leather in our tests.

Feed control.—This test was conducted on 12 cabretta skins. Based on drained pickled weight, the procedure was as follows:

Pickled skins (6300 g.)	100%
Water	100%
NaCl	6%
Glutaraldehyde (25% aqueous solution)	4%
Drum ½ hour, pH 2.3	
Add sodium acetate (anhyd.)	6%
Drum 1 hour, pH 5.0, Ts 77°C.	
Add glutaraldehyde 25% solution)	8%
Drum 6 hours, pH 5.0, Ts 84°C.	
Wash ½ hour	
Drain	

pH control—This test was carried out with 3 cabretta skins according to the following procedure:

Pickled skins (2115 g.)	100%
Water at 90°F.	100%
NaCl	6%
Glutaraldehyde (25% aqueous solution)	12%
Drum ½ hour, pH 2.3	
Add sodium formate (anhyd.)	4%
Drum 2 hours, pH 4.0, Ts 79°C.	
Add $NaHCO_3$	3%
Drum 1½ hours, pH 6.6	
Add $NaHCO_3$	0.5%
Drum 2 hours, pH 7, Ts 82°C.	
Add formic acid (90% solution)	1.75%
Drum ½ hour, pH 4.4	
Wash ½ hour, Ts 83°C.	

DISCUSSION

The preceding paper (1) presented data showing that glutaraldehyde was an unusual aldehyde with regard to its tanning properties. The present study shows that the leather also exhibits some unusual properties in comparison to conventional aldehyde leathers such as formaldehyde and glyoxal. The data discussed below were obtained for 24-hour tannages with the laboratory drum turning intermittently overnight.

No difficulty with the glutaraldehyde leather was experienced in the fatliquoring and other usual posttanning operations given the regular chrome garment leather. Soft, mellow leather of a pleasing character was obtained from every test which covered the pH range from about 2.5 to 10, and with concentrations of glutaraldehyde (100% basis) as low as 1.5%. Consumption of aldehyde (Table I) becomes practically quantitative in the pH region above 6.

The shrinkage temperature of these aldehyde leathers was lowered slightly by the conventional posttanning operations given chrome garment leather. However, the shrinkage temperature of the glutaraldehyde-tanned leathers was as high as, or higher than, those leathers tanned with formaldehyde or glyoxal under comparable conditions. As judged by the tanner, glutaraldehyde produced leather far superior in appearance and feel to that from formaldehyde or glyoxal.

It was hoped that analysis of the leather would enable calculation of fixed aldehyde from the balance remaining over and above the hide substance, fat, and ash. Unfortunately the finishing operation, such as syntan bleach used on the regular leather, apparently contributed added fixed substances,

as is evident from the high balance figures for the formaldehyde-tanned leathers (Table I). Direct determination of formaldehyde in the finished leather by the method of Highberger and Retzsch (10) gave values of 0.20, 0.37, and 0.60% formaldehyde (MFB) for the leathers in tannage Nos. 20, 22, and 23, respectively (Table I). This data expressed as millimoles per gram of hide substance gave fixed formaldehyde contents of 0.11, 0.18, and 0.28, respectively. These values are considerably less than formaldehyde fixed by the skin in equilibrium with the tanning liquor (column 12, Table I) as calculated from aldehyde consumed during tanning. This difference is most likely accounted for by the reversible nature, at least in part, of the tannage. Unfortunately, a method for the direct determination of glutaraldehyde in leather is not unavailable, and comparison of the reversible nature of these two tannages is not possible. It is interesting to note that fixation of these two aldehydes at equilibrium, as calculated from aldehyde consumed during tanning under similar conditions, was very near the same (compare last column of Table I for tannage Nos. 6, 15, and 18 with 20, 22, and 23). Fixed aldehyde at equilibrium varied from about 0.82 to 1.18 millimoles per gram of hide substance in the pH range studied, i.e., 5.0 to 9.4.

Various properties of the finished leathers are summarized in Table II. This stitch-tear data were collected on a limited number of specimens. However, the data indicate reasonably satisfactory strength properties.

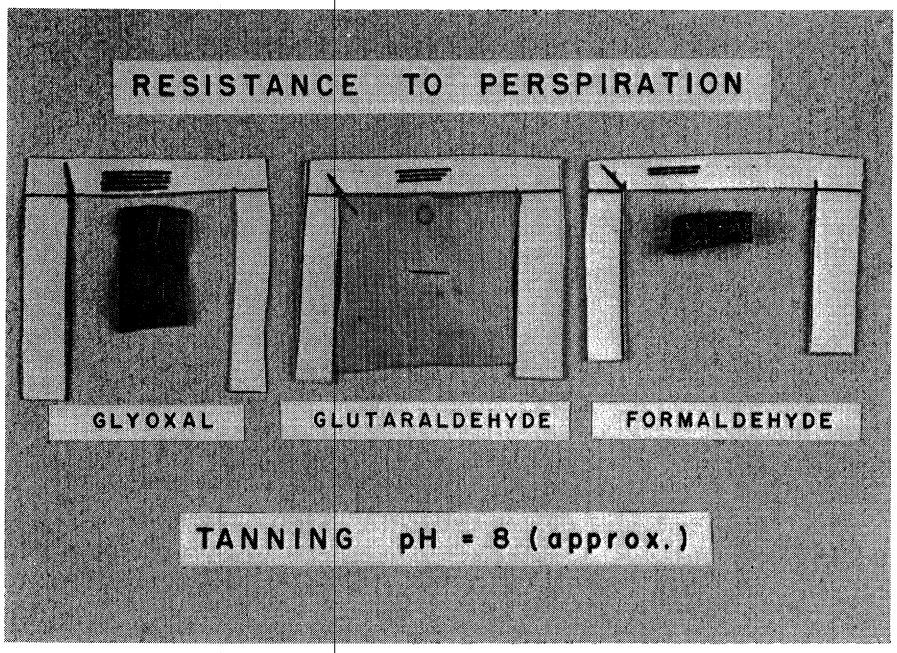

FIGURE 1.—Photograph of test specimens of glyoxal, glutaraldehyde, and formaldehyde sheepskin leathers after perspiration test.

The bar graph (Fig. 2) shows at a glance the influence of various tanning factors on the perspiration resistance of glutaraldehyde-tanned sheepskins.

The resistance of the glutaraldehyde tannage to hot soap solution also was determined in order to evaluate the tannage from a washability standpoint. In this instance the change in shrinkage temperature of the leather was used as a criterion of stability. After the test, the specimens were examined for leather characteristics. The results in comparison with formaldehyde were not so marked as in the case of the perspiration test. The data (Table II) indicated that glutaraldehyde leather was more resistant to "detannage" than the corresponding formaldehyde or glyoxal leathers. Only at the highest pH of tannage (9.5 to 10) was the shrinkage temperature of the washed formaldehyde leather comparable to that in the case of glutaraldehyde. In the tannages carried out at lower pH the glutaraldehyde leathers were distinctly more resistant to lowering of the shrinkage temperature by hot soapy water. All the washed leathers were firmer after drying than the unwashed samples. However, a slight mechanical action readily restored the soft flexible character to the glutaraldehyde-tanned leathers.

A 24-hour tannage is not practical for commercial drum tanning. In tests of the glutaraldehyde tannage with small packs it was found that with the drum at rest overnight streaks of color developed on the surface of the leather. The rate studies in the previous paper (1) clearly show that tanning can be accomplished in much less than 24 hours and that overnight tannage is not necessary. In fact under some conditions tanning with glutaraldehyde appears to be complete in one or two hours. However, if tanning is carried out too rapidly, drawn grain is obtained. This can be avoided by proper control, such as adding the glutaraldehyde in several feeds or by careful regulation of the pH when the aldehyde is added in one feed. The two procedures listed in the Experimental section under "Eight-Hour Tannages" illustrate these methods of control and were found satisfactory for avoiding drawn grain in tanning of sheepskins in the laboratory.

With regard to pH control it was found that a pH of approximately 4.2 was critical to prevent drawn grain when all the glutaraldehyde at the 12% level was added in one feed. Sodium formate was an excellent buffer which provided almost automatic control just below the critical pH. One or two hours tanning at this pH permitted sufficient fixation so that drawn grain was avoided upon subsequent elevation of pH. A shrink test in the early stages of tanning was helpful in determining suitable tanning procedures. Drawn grain was avoided if the tanning was carried out under conditions such that the Ts reached the neighborhood of 70° to 75 °C. in the first hour or two.

These observations were made on small packs of sheepskins tanned under laboratory conditions. Some adjustments may be necessary to arrive at optimum conditions with other raw stock and in full pack tests. The rapid

tanning action of glutaraldehyde is a property that may be of interest in producing textured grain leather.

Completion of the tannage within eight hours, including removal of unused glutaraldehyde by washing, completely eliminated the problem of streaked leather. The leathers tanned in eight hours showed substantially the same properties as those tanned for 24 hours.

Because of its ability to tan over a wide pH range, glutaraldehyde was found to be compatible in combination tannages with other conventional tanning agents, with an enhancement of leather properties.

REFERENCES

1. Fein, M. L., Harris, E. H., Jr., Naghski, J., and Filachione, E. M. *JALCA*, **54**, 488 (1959).
2. ALCA Provisional Method J1, April, 1953.
3. Colin-Russ, A. *J. Intern. Soc. Leather Trades' Chemists*, **31**, 329 (1947).
4. *Year Book of the American Association of Textile Chemists and Colorists*, 1947–1948, p. 102. Test No. II: Colorfastness of Textiles to Commercial Laundering and Domestic Washing.
5. ALCA Provisional Method E13, April, 1953.
6. Willits, C. O., and Ogg, C. L. *J. Assoc. Offic. Agr. Chemists*, **33**, 179 (1950).
7. ALCA Provisional Methods B3 and B15, June, 1957.
8. Koppenhoefer, R. M. *JALCA*, **32**, 627 (1932).
9. ALCA Provisional Method B4, June, 1957.
10. Highberger, J. H., and Retzsch, C. E. *JALCA*, **33**, 341 (1938).
11. Bowes, J. H., in *Progress in Leather Science*: 1920–1945 (London: British Leather Manufacturers' Research Assoc., 1948) Chap. 25, p. 515.
12. Nayudama, Y., Jayaraman, S. K., and Krishnan, T. S. *JALCA*, **52**, 238 (1957).

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DISCUSSION

DR. LUDWIG SELIGSBERGER (Quartermaster Research and Engineering Center): The experiments and observations of Dr. Filachione, I think, should enable chemists in any industrial laboratory to employ glutaraldehyde intelligently and to learn by themselves what they can do with the material.

The authors who share the honor of this type of painstaking study—I am thinking here particularly of following the pickup of the aldehydes quantitatively over an extended period of time—are to be warmly commended. It is also gratifying to know that the work was done mostly on whole skins and that we can inspect the leather produced.

The most impressive result, in my opinion, is the speed of the glutaraldehyde fixation. The reason, I think, is because glutaraldehyde is monomeric in the 25% commercial solution, whereas glyoxal and formaldehyde are more

or less aggregated at the concentrations employed, and the aggregated portion returns to the monomeric form gradually after dilution in the tanning drum. The question of whether the monomeric forms differ in their rate of tanning is theoretical but may one day be answered by a properly designed laboratory experiment.

It was rather unexpected for me to see that the shrinkage maxima for all three aldehydes were lower than in some experiments I conducted on cowhide side leather. The difference was lowest with glutaraldehyde and somewhat higher with formaldehyde. We know from the literature that we can reach 90° or 91°C. with formaldehyde and that we can also reach 89° or 90°C. with glyoxal under proper conditions. That is why I think that the laundering and perspiration tests with those two aldehydes are not as conclusive as they are with glutaraldehyde. It may be possible to get about the same results, but I have no data to prove that.

I also want to mention that in some experiments I conducted, I got a brown color on the outside of the glutaraldehyde, but the inside was light—very light, almost white.

DR. PETER R. BUECHLER (Rohm & Haas Co.): I was very much interested in the observation that this leather is more resistant to perspiration, because one of the difficulties with formaldehyde-tanned leather, as commercially made, is the difficulty in drying out that leather without getting shrinkage. I wonder if you have any comparative data to indicate whether or not glutaraldehyde-tanned leather will give a better area yield on drying after tannage.

DR. FILACHIONE: You mean a better area yield than formaldehyde-tanned skin?

DR. BUECHLER: Yes.

DR. FILACHIONE: No, we have no data along that line.

Incidentally, in connection with Dr. Seligsberger's comments, I think he is absolutely right that you could expect a shrink temperature of around 90°C. for formaldehyde leather. However, the sheepskins that we used had a shrink temperature in the untanned state of around 50°C., which is about 10° lower than that usually observed for cowhide. For this reason the Ts would not be elevated as high in the case of these sheepskins as it would with other stock, such as cowhide.

In our tests with sheepskins the color of the tanned skin was fairly uniform throughout the thickness. As the pH of tanning was increased we got more color developed in the leather, but it was more or less distributed throughout the thickness.

One of these leather jackets that I have here is finished in the natural color and you will see it is a light, cream-colored leather.

DR. SOMERVILLE: How does this tannage behave as regards coloring dyestuffs and fatliquoring?

DR. FILACHIONE: We don't have too much data on its behavior to dyestuffs. One of these jackets is in charcoal gray. The leather accepted this color very well. In another case we have seen a piece of chrome-tanned leather and one of glutaraldehyde-tanned leather which were colored together with a red dye. The glutaraldehyde leather was considerably brighter in color than the chrome leather. In fact, the chrome-tanned leather looked orange-colored compared to the bright red color of the glutaraldehyde specimen.

With regard to fatliquoring, they were given the regular fatliquor that is given to the chrome-tanned leather. The tanner reported no difficulty; in fact he thought the fatliquor was very uniformly distributed in the leather.

MRS. JEAN TANCOUS (University of Cincinnati): Would it be considered a washable leather?

DR. FILACHIONE: I should emphasize that we have only preliminary data. We think they indicate the comparative stability of the tannage to washing. We have put regular chrome-tanned garment leather through the same wash test, and the shrinkage temperature went down considerably more than did the glutaraldehyde-tanned leather. Even though the chrome-tanned leather was initially at a higher shrinkage temperature than the glutaraldehyde leather, after the third wash its shrinkage temperature was below that of the glutaraldehyde.

RICHARD N. JONES (A. C. Lawrence Leather Co.): Which one of the four A.A.T.C.C. tests was used? Specifically, what temperature and soap concentration?

DR. FILACHIONE: We used the test corresponding to A.A.T.C.C. Method No. 2. The specimens were washed in a 0.5% soap solution at 120°F. for ½ hour.